Message

From: Culpepper, Linda [linda.culpepper@ncdenr.gov]
Sent: 7/31/2019 12:01:04 PM
To: Strynar, Mark [Strynar.Mark@epa.gov]
Subject: RE: [External] RE: Notes from call Friday, July 19, 2019 - Non-Targeted analysis and characterization sampling plans

Thank you for the quick confirmation, Mark!

linda

Linda Culpepper
Director, Division of Water Resources
North Carolina Department of Environmental Quality

1611 Mail Service Center
Phone: 919-707-9014

From: Strynar, Mark <Strynar.Mark@epa.gov>
Sent: Wednesday, July 31, 2019 7:27 AM
To: Culpepper, Linda <linda.culpepper@ncdenr.gov>; Sivertsen, Scott <Sivertsen.Scott@epa.gov>; Martin, Allen D <Allen.Martin@ncdenr.gov>
Cc: Aker, Sandra <Aker.Sandra@epa.gov>
Subject: RE: [External] RE: Notes from call Friday, July 19, 2019 - Non-Targeted analysis and characterization sampling plans

Linda,

I agree with Scott on both counts.

A better solvent than water is needed. However regardless of the solvent chosen the same loss experiments need to be conducted.

On the direct injection method, if it shows similar sensitivity and performance I am all for it. I am moving in this direction myself.

Mark

From: Culpepper, Linda <linda.culpepper@ncdenr.gov>
Sent: Tuesday, July 30, 2019 4:14 PM
To: Sivertsen, Scott <Sivertsen.Scott@epa.gov>; Martin, Allen D <Allen.Martin@ncdenr.gov>; Strynar, Mark <Strynar.Mark@epa.gov>
Cc: Aker, Sandra <Aker.Sandra@epa.gov>
Subject: RE: [External] RE: Notes from call Friday, July 19, 2019 - Non-Targeted analysis and characterization sampling plans

Thank you, Scott.

Mark – unless you think differently, we'll move forward indicating water is a not approved as the solvent for stock standards,
and they need to meet an MRL comparable to the private labs. GEL's RL is <2 ppt for some and <4 ppt for others.

linda

Linda Culpepper
Director, Division of Water Resources
North Carolina Department of Environmental Quality

1611 Mail Service Center
Phone: 919-707-9014

From: Sivertsen, Scott <Sivertsen.Scott@epa.gov>
Sent: Tuesday, July 30, 2019 1:52 PM
To: Culpepper, Linda <linda.culpepper@ncdenr.gov>; Martin, Allen D <Allen.Martin@ncdenr.gov>; Strynar, Mark <Strynar.Mark@epa.gov>
Cc: Aker, Sandra <Aker.Sandra@epa.gov>
Subject: RE: [External] RE: Notes from call Friday, July 19, 2019 - Non-Targeted analysis and characterization sampling plans

Hi Linda,

Below are my thoughts on the two topics you brought up. These are essentially repeats of the comments I submitted on July 5. Feel free to use them as you see fit in any response you may submit to Chemours.

Stability Study

The purpose of the study is to address questions regarding the stability of aqueous PFAS standards over time, using time and temperature as variables. If stock standards (which will be used to calibrate instrumentation) are in the same solvent system as the samples, and both calibrant and sample are degrading at the same rate, no degradation will be quantified. I've brought it up multiple times in comments to Chemours; I don't think water is a viable solvent for stock standards. It seems like a poorly designed experiment from that perspective. If non-targeted analyses are performed and previously unseen compounds develop over time, it would be an indicator of degradation but seems like an overly complex way to quantify degradation of the compounds under study.

In my opinion, water as a solvent for stock solutions is unacceptable until it is demonstrated that concentrations of standards do not change over time. I don't know if it's possible for Chemours to shift their solvent system from aqueous to organic. Mark and Allen may have a better understanding of their processes for synthesis and solvation of the compounds. Chemours has stated that this study will evaluate water as a storage solvent, but I don't see how any degradation can be elucidated given the current design which uses water in all solutions.

Direct Injection vs. SPE

Direct injection (which the Region 4 and 5 labs routinely use) is an acceptable technique. The biggest determinant for deciding between direct injection and solid phase extraction (SPE) is the required minimum reporting level (MRL). If the

instrumentation used for determinative analysis lacks the required sensitivity to attain the required MRL, a sample concentration step (e.g., SPE) is required. SPE has the advantage of driving MRLs lower, by orders of magnitude, due to the sample enrichment conferred by the technique. Also, SPE may have some cleanup properties associated with it. Direct injection has the advantage of simplified sample handling. Throughput is increased and the potential for contamination from sample manipulation is reduced. With either technique, aliquoting of the samples is not allowed, because of the potential for sorption to the sample container surfaces which has the potential of creating a nonrepresentative sample. Procedural calibration standards would address the issue of sorption, however, I don't believe that has been proposed.

Best,

Scott

From: Culpepper, Linda <linda.culpepper@ncdenr.gov>
Sent: Wednesday, July 24, 2019 10:20 PM
To: Sivertsen, Scott <Sivertsen.Scott@epa.gov>; Martin, Allen D <Allen.Martin@ncdenr.gov>; Strynar, Mark <Strynar.Mark@epa.gov>
Subject: RE: [External] RE: Notes from call Friday, July 19, 2019 - Non-Targeted analysis and characterization sampling plans

Gentlemen – we are at a point where we can give a directive on what is needed, and we need to provide Chemours with a written response
(can take the form of an approval letter, an approval with stipulations, tentative approval pending outcome of a study, etc.).

- Want to check in on whether their study effort for the lab standards solvated in water is an acceptable approach, or should we direct them right now to shift to the solvent system?

- Also, is the direct injection acceptable or do we require the solid phase extraction method now? My understanding is that
their contract lab is using the direct injection method based on Chemours' specification to them, and in the lab's work for other
clients the lab uses the extraction method. If I have misunderstood this aspect, please advise.

Any other items that are not resolved in your perspective and you believe should be contemplated in a directive or tentative approval?
Appreciate your time and expertise working with these issues!!!

Linda

Linda Culpepper
Director, NC DEQ Division of Water Resources

Email: linda.culpepper@ncdenr.gov
Phone: 919-707-9014

From: Sivertsen, Scott <Sivertsen.Scott@epa.gov>
Sent: Wednesday, July 24, 2019 12:47 PM
To: Garon, Kevin P <Kevin.Garon@chemours.com>; Martin, Allen D <Allen.Martin@ncdenr.gov>; Strynar, Mark <Strynar.Mark@epa.gov>; Leung, Lam-Wing H <LAM.H.LEUNG-1@chemours.com>; Culpepper, Linda <linda.culpepper@ncdenr.gov>

Cc: Compton, Christel E <CHRISTEL.E.COMPTON@chemours.com>
Subject: [External] RE: Notes from call Friday, July 19, 2019 - Non-Targeted analysis and characterization sampling plans

I have a clarification of comment #2, below. My concern is not so much with compound stability and conversion to other compounds, but rather their solubility in water and surface adsorption to containers. This concern is inclusive of the stock standards and any dilutions of those primary solutions: if standards are solvated in water without an adequate organic co-solvent, the potential for surface activity and binding to the container is possible. That causes dissolved concentrations to change introducing low bias. The phenomena is more likely with longer chain-length PFAS but should be investigated for the Table 3+ compounds. Lam also acknowledged the concern of water as a solvent for the stock standards.

This is the reason that in direct injection analyses all solutions are kept in 50% or greater organic solvent.

My written comment, which was paraphrased during the call:

The Chemours standards are the only PFAS standards which I am aware of in which the stock solutions are solvated in water. Commercially, PFAS standards are typically found in basic methanol, to prevent (1) esterification and (2) sorption to the standard vial. Studies of legacy PFAS have shown that they are surface active and without the addition of organic solvent, losses to the container walls are seen over time. Without data to support water as a solvent system, in my opinion it is inadequate as a solvent.

That was in response to Chemours comment #4 from the document Para 11 Response to Comments 2019.06.18.pdf, which stated:

The Table 3+ standard materials are provided by Chemours in water as the solvent. Additional water is not added by the commerical laboratories. Dilutions with methanol are made to achieve a 50/50 water/methanol solution which is required for the chromatographic conditions at the beginning of the chromatographic run; it is not performed to keep the analytes in solution. The commerical laboratories have not observed any indication suggesting the the Table 3+ compounds in the standards provided by Chemours are unstable or subject to adsorption losses, as the stored solutions are used repeatedly and they observe no change in expected concentrations over time. Chemours is planning to undertake a study to evaluate the stability of aqueous PFAS standards over time and under different storage conditions. The Stability Testing Work Plan has been provided to NCDEQ as Attachment 1 of this Response to Comments document.

Regards,

Scott

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Scott Sivertsen
Chemist, Region 4 US EPA
980 College Station Road
Athens, GA 30605

706/355-8869 (office)
706/355-8857 (FAX)
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From: Garon, Kevin P <Kevin.Garon@chemours.com>
Sent: Monday, July 22, 2019 4:32 PM
To: Martin, Allen D <Allen.Martin@ncdenr.gov>; Strynar, Mark <Strynar.Mark@epa.gov>; Sivertsen, Scott

<Sivertsen.Scott@epa.gov>; Leung, Lam-Wing H <LAM.H.LEUNG-1@chemours.com>; Culpepper, Linda <linda.culpepper@ncdenr.gov>
Cc: Compton, Christel E <CHRISTEL.E.COMPTON@chemours.com>
Subject: Notes from call Friday, July 19, 2019 - Non-Targeted analysis and characterization sampling plans

Allen,
I took the liberty of drawing up some notes from our call last Friday. Please see below:

Notes from Friday, July 19, 2019 teleconference meeting, 10:00am with:

Allen Martin
Scott Sivertsen
Mark Strynar
Lam-Wing Leung
Kevin Garon

Purpose:
To discuss comments on Chemours submittals of workplans under Paragraph 11a and 11b of the Consent Order, and multiple comments and response to comments between Chemours and DEQ/EPA.

Focus of call (main comments as presented by Scott Sivertsen):
1) Scott expressed concern about having Chemours prepare the only set of standards for the Table 3 compounds. He expressed concern that the standards were not as pure as he would like, and would like to see Chemours get standards from 3rd parties. Lam responded that because these compounds are generally Chemours specific and are generally generated as byproducts of manufacturing (as opposed to manufacturing the compound itself), Chemours had to synthesize these chemicals in order to prepare standards. Up until recently there were no other labs that could make these standards. Lam has since found that 12 of the 24 Table 3+ compounds now have standards that are made by 3rd parties. Lam prepared and submitted a list of the 24 compounds and who and where standards can be obtained. He also indicated that he expected 3rd parties to continue to create standards for the remaining 12 compounds. In the meantime, Chemours will continue to provide these standards. Allen Martin asked Lam for a set of standards and later sent a shipping address. Lam will follow-up by sending a full set of standards to Allen at the addressed he requested.

2) Scott expressed concerns and asked questions about the stability of all the PFAS compounds in glass bottles with a focus on long-term storage and also the potential impact of temperature in long-term storage. Lam responded that Chemours proposed to DEQ and has recently begun work on stability testing. Chemours stores all sample retainage in their sample bottle in a refrigerator for potential reanalysis. Chemours does not think that the sample bottle or temperature at storage will impact results due to sorption to the sample container, or reaction to temperature. However, Chemours is currently running sample stability tests to analyze these potential impacts.

3) Scott had questions on MRL and/or LLQ verification spikes to demonstrate lab MRL's. Lam has prepared the following response: For the Table 3+ analysis, laboratories are directed to report results to an LOQ as a reporting limit. Laboratories are requested to establish an LOQ that is based on a low calibration standard or standard equivalent concentration not to exceed 0.002-0.02 ug/L (for some of the early eluters, the LOQ might be higher but they are no longer on the Table 3+ method list). The LOQ for wastewater samples may exceed this level. Reporting limits may vary from sample to sample in accordance with standard laboratory practices (e.g., dilution resulting from high analyte concentration).

The laboratories are requested to perform MDL studies in accordance with 40CFR136 at least semiannually to ensure that the low calibration standard equivalent concentration is above the EPA protocol MDL. The MDL determination will be for information only. Sample results will be reported to the LOQ with non-detect results shown as <LOQ. We will continue to work with our testing labs to improve upon the testing method(s).

4) Scott had questions and comments on the aliquoting of samples. This concern also gets to the potential of sorption of compounds to the sample jar. Scott indicated that EPA takes a 5 cc sample for analysis. Chemours collects a 250 cc sample. The reason Chemours collects a large sample is to hold for additional analysis as needed. Chemours protocol also is to run a sample, then run a spiked sample, then run the sample again (which takes more sample volume). The concern here is related to the same as in comment #1 which is the potential for certain PFAS constituents to sorb to the sample container. Chemours response is that we have initiated a stabilization testing program to determine if sorption of PFAS to sample containers is in fact an issue or not. Chemours proposes to wait for the results of the stability testing before making any changes to its proposed work plans.

Thanks for your time last Friday. Please review and let me know if I missed anything or mischaracterized our conversations in any way. We can certainly make ourselves available for an additional teleconference if necessary.

Thanks,
Kevin